

# Simple Lattice-Models of Ion Conduction: Counter Ion Model vs. Random Energy Model

J. Reinisch and A. Heuer

*Westfälische Wilhelms-Universität Münster  
Institut für Physikalische Chemie and SFB 458  
Schlossplatz 4/7, 48149 Münster, Germany*

(Dated: February 1, 2008)

The role of Coulomb interaction between the mobile particles in ionic conductors is still under debate. To clarify this aspect we perform Monte Carlo simulations on two simple lattice models (Counter Ion Model and Random Energy Model) which contain Coulomb interaction between the positively charged mobile particles, moving on a static disordered energy landscape. We find that the nature of static disorder plays an important role if one wishes to explore the impact of Coulomb interaction on the microscopic dynamics. This Coulomb type interaction impedes the dynamics in the Random Energy Model, but enhances dynamics in the Counter Ion Model in the relevant parameter range.

PACS numbers: 66.30.Dn

## I. INTRODUCTION

Many disordered insulating materials show universal behavior in their ionic DC- and AC-conductivity. Two prominent examples are the Arrhenius temperature dependence of the DC-conductivity and the fact that AC-conductivity data for different temperatures can be scaled onto a single master curve. This curve is similar for most materials. This observed universality [1, 2] has stimulated researches to find a common mechanism for ion conductivity in these materials. A different type of system are disordered Anderson insulators, displaying electron transport. They are denoted Coulomb glasses. In contrast to ion conductors non-localized dynamical processes play an important role in these systems. The non-localized dynamics give rise to a very different temperature dependence of the DC-conductivity at low temperatures, which turns out to be proportional to  $\exp[-(T_M/T)^{1/4}]$  (Mott's law [3]) or to  $\exp[-(T_0/T)^{1/2}]$  (Efros-Shklovskii law [4]).

Similar computational approaches have been chosen to investigate both types of problems and various theoretical models have been developed in this context

[5, 6, 7, 8, 9, 10]. The focus of this work lies on the effect of Coulomb interaction on the microscopic dynamics in ion conductors. We chose two similar lattice models to investigate the relevant microscopic dynamics: The Counter Ion Model (CIM) [11, 12] and the Random Energy Model with cation-cation interaction (REM) [13], which has some features in common with the Coulomb glass model used for the second group of disordered solids [9, 10]. The CIM and the REM are designed to reflect important aspects of vitreous ion conductors, which are a high degree of disorder and mobile charged ions in a fixed glass network. The models differ in the way how the time independent (static) disorder is realized. In this paper we analyze the effects of Coulomb interaction among mobile ions and show that the nature of the disorder has great influence on the dynamics. In Sect. II we present the models as well as computational details, while in the Sect. III the results are presented and discussed.

## II. MODELS AND COMPUTATIONAL DETAILS

### A. Similarities of both models

Both models base on a single type of mobile particles restricted to discrete sites in a simple cubic lattice with  $l^3$  sites of distance  $a$ . The distance for a single jump is limited to  $a$ , and occupied positions are forbidden. All mobile particles have the same positive charge. In contrast to other works on the CIM [11, 12] the strength of the Coulomb interaction between the mobile particles can be varied independently from the strength of static disorder by appropriate selection of parameters, as it is also possible for the REM; see below for precise definitions. This variation is essential to elucidate the effect of Coulomb interaction among the mobile particles on their dynamics. There are two energy contributions to the total Hamiltonian: Mobile particles moving on a time dependent potential surface (generated by the particles

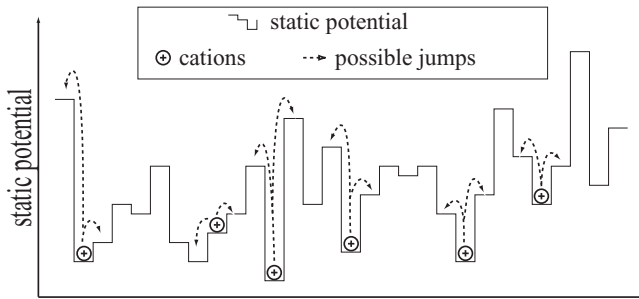


Figure 1: One dimensional illustration of the static potential landscape in the random energy model. The arrows indicate possible jumps.

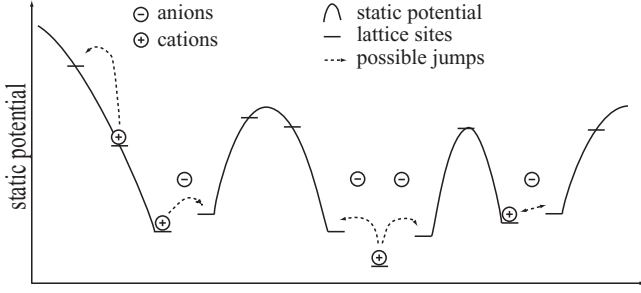


Figure 2: One dimensional illustration of the static potential landscape in the counter ion model. The arrows indicate the possible jumps.

themselves) and on a time independent potential surface. We call the first dynamic and the latter static. The dynamic part has the same form in both models and the Hamiltonian for the cation-cation interaction is,

$$H_{cat} = \frac{1}{2} \sum_{i \neq i'} \frac{n_i n_{i'} e^2}{r_{ii'}}. \quad (1)$$

A configuration with sites  $i$  is described by the occupation numbers  $n_i = 1$  for occupied sites and  $n_i = 0$  for empty sites. The omitted factor  $4\pi\epsilon_0$  is taken in account by use of appropriate units. The mean nearest-neighbor interaction in a system with randomly distributed cations can be written as

$$V_c = \frac{e^2}{r_s}. \quad (2)$$

$r_s$  is the mean distance of nearest neighbors in such a system with cation-concentration  $c = N/l^3$ ,

$$r_s = \sqrt[3]{\frac{3}{4\pi c}}. \quad (3)$$

Furthermore we introduce the dimensionless parameter  $\Gamma_{cat}$  via

$$\Gamma_{cat} = \frac{V_c}{k_B T} = \frac{e^2}{k_B T r_s}. \quad (4)$$

In the literature this parameter is already established for the REM [13] and we use it for the CIM to ensure comparability. The Hamiltonian for the cation interaction can thus be rewritten as,

$$\frac{H_{cat}}{k_B T} = \Gamma_{cat} \cdot \frac{H_{cat}}{V_c}. \quad (5)$$

In what follows  $V_c$  is regarded as a constant for a given concentration. Here  $\Gamma_{cat} \propto e^2$  is a measure for the interaction strength between the cations relative to  $k_B T$ .

## B. Static Disorder in the Random Energy Model

The REM features a straightforward approach of the principle of representing complexity by randomness.

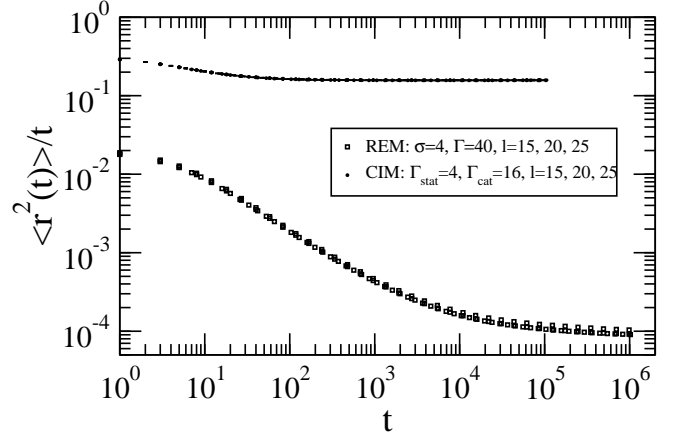


Figure 3: Typical errors and finite size effects for both models. The largest errors are of the size of the symbols and occur at large  $t$ .

Each site  $i$  gets a random energy taken from a Gaussian distribution with standard deviation  $\sigma_\epsilon$  and mean value 0. The Hamiltonian for the static disorder becomes,

$$H_{stat} = \sum_i n_i \cdot E_i^{static}. \quad (6)$$

The model is fully determined by two dimensionless parameters:  $\sigma_r$  is connected to the standard deviation of the random site energies by,

$$\sigma_r = \frac{\sigma_\epsilon}{k_B T}. \quad (7)$$

In changing  $\sigma_r$  one can change the strength of static disorder relative to temperature in the system. As before, the second parameter  $\Gamma_{cat}$  determines the cation-cation interaction strength. The total Hamiltonian reads,

$$\frac{H}{k_B T} = \Gamma_{cat} \cdot \frac{H_{cat}}{V_c} + \frac{H_{stat}}{k_B T}. \quad (8)$$

In Fig. 1 the potential landscape of the REM is illustrated.

## C. Static Disorder in the Counter Ion Model

In the CIM static disorder is generated by randomly placing negatively charged particles at centers of cubic lattice cells. As for cations these anions cannot occupy the same site. The resulting potential landscape (see Fig. 2) is different from that seen in Fig. 1. As for the REM we used  $\Gamma_{cat}$  to control the interaction strength among cations and defined a parameter  $\Gamma_{stat}$  adequate to control the interaction strength between cations and anions. It is defined in analogy to  $\Gamma_{cat}$  as,

$$\Gamma_{stat} = \frac{k_{ca} \cdot V_c}{k_B T}. \quad (9)$$

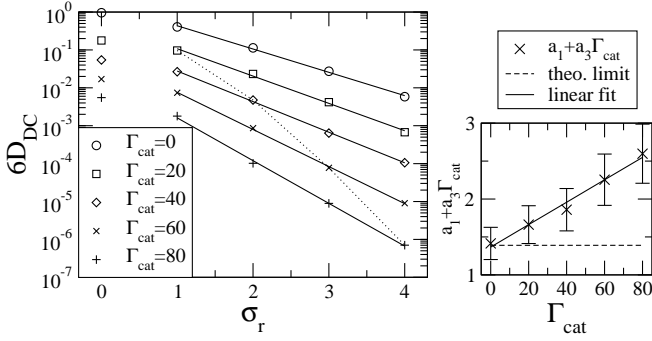


Figure 4: Left: Dependency of the low frequency diffusion constant  $D_{DC}$  on  $\sigma_r$  in the REM. The lines correspond to exponential fits, the data for  $\sigma_r = 0$  are omitted. The dotted line describes the temperature dependency of  $D_{DC}$  for a constant quotient  $\frac{\sigma_r}{\Gamma_{cat}} = \frac{\sigma_e}{V_c} = 0.05$ . The errors are smaller than the symbol size.

Right: Dependency of the slope on  $\Gamma_{cat}$ . The data match the theoretical limit at  $\Gamma_{cat} = 0$ .

The factor  $k_{ca}$  has been introduced to vary the strength of the cation-anion interaction separately from the cation-cation interaction. For  $k_{ca} = 1$  and thus  $\Gamma_{cat} = \Gamma_{stat}$  one recovers the standard choice of parameters for the CIM. In contrast to previous works we wish to break with charge neutrality and rather interpret  $H_{stat}$  as a general static disordered energy landscape. Thus  $\Gamma_{stat}$  can be varied in analogy to  $\sigma_r$  thereby modifying the strength of the disorder. The total Hamiltonian for the CIM is,

$$\frac{H}{kBT} = \Gamma_{cat} \cdot \frac{H_{cat}}{V_c} + \Gamma_{stat} \cdot \frac{H_{stat}}{V_c}. \quad (10)$$

#### D. Computational Settings

The number of lattice sites in one dimension was set to 20 for all data throughout this work. For simulating bulk properties we apply periodic boundary conditions and the minimum image convention [14]. As shown in in Fig. 3 the smallness of the finite size effects justifies our choice of 20 lattice sites per dimension. All presented data were calculated with a cation concentration of 0.03. The number of anions for generating the static energy landscape in the CIM was kept identical to the number of cations. The contributions of the Coulomb interaction were calculated via Ewald summation. The number of different starting configurations ranges from 5 to 10. This rather small number made it possible to simulate a large range of parameters. For model systems with  $c = 0.03$  and  $e^2 = 1$ , which were used throughout this paper, one has  $V_c = 0.501$ .

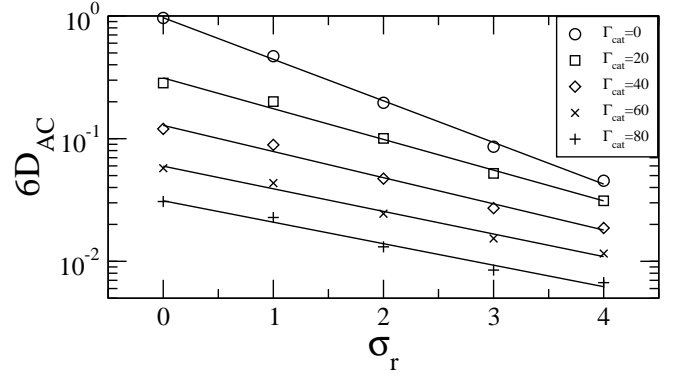


Figure 5: Dependency of the high frequency diffusion constant  $D_{AC}$  on  $\sigma_r$  in the REM. The lines are exponential fits and serve as guides to the eye. The errors are within the symbol size.

### III. RESULTS

The diffusion constants are taken from  $\langle r^2(t) \rangle / t$ -data. Fig. 3 shows some examples. Each curve begins with a short-time plateau changes into a dispersive regime from  $t_1$  to  $t_2$  and forms a long-time plateau beyond  $t_2$ . In the dispersive regime between  $t_1$  and  $t_2$  the curve follows a Jonscher type [15] power law

$$\langle r^2(t) \rangle / (6t) \sim t^{k'-1} \quad (11)$$

The following relations are used to determine the diffusion constants,

$$\begin{aligned} 6D(t) &= \langle r^2(t) \rangle / t, \\ 6D_{DC} &= \lim_{t \rightarrow \infty} \langle r^2(t) \rangle / t, \\ 6D_{AC} &= \lim_{t \rightarrow 0} \langle r^2(t) \rangle / t. \end{aligned}$$

The high frequency diffusion constant  $D_{AC}$  was also calculated from the average hopping rate  $a^2 \langle w \rangle = 6D_{AC}$ . For details on the general behavior of the REM and the CIM, see [12, 13, 16].

In the REM the presence of cation-cation interaction leads to a significant decrease in diffusion and an increase in dispersion [13]. A quantitative analysis of the behavior can be found in [17]. For a REM without long range Coulomb interaction, i.e.  $\Gamma_{cat} = 0$ , the activation energy  $E_a$  can be calculated as the difference between the Fermi energy and the critical percolation energy [7, 17]. For a concentration of 0.03 the Fermi energy is  $-1.88\sigma_e$  and the percolation energy is  $-0.49\sigma_e$ . Hence the activation energy is  $-0.49\sigma_e + 1.88\sigma_e = 1.39\sigma_e$ . This reasoning is only valid for low temperatures  $\sigma_r \gg 1$ . For high temperatures  $\sigma_r \ll 1$  it can be shown [17] that the activation energy is roughly equal to  $\sigma_e / \sqrt{\pi} = 0.56\sigma_e$ . Here we analyze the REM including long range Coulomb interaction for which this analytical treatment is no longer possible. Simulated data for various  $\Gamma_{cat}$  and  $\sigma_r$  are shown in Fig. 4(left). The data for  $\Gamma_{cat} = 0$  correspond to vanishing cation-cation interaction and the regression for the

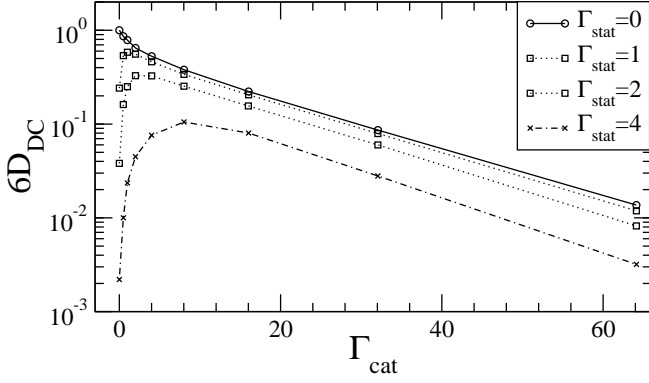


Figure 6: Dependency (CIM) of the low frequency diffusion constant  $D_{DC}$  on  $\Gamma_{cat}$ . The maximum ( $\Gamma_{cat,max}$ ) shifts to larger  $\Gamma_{cat}$  for higher values of  $\Gamma_{stat}$ . The errors are smaller than the symbols.

low temperature regime leads to an activation energy of  $1.41\sigma_\epsilon$  which is in good agreement with the theoretical value resulting from percolation arguments, see above. One can easily see that the low temperature part of all curves can be approximated fairly well by straight lines. The first data point for  $\sigma_r = 0$  is omitted for all  $\Gamma_{cat}$ . Interestingly, the change of slope at high temperatures, i.e. small  $\sigma_r$ , as predicted for  $\Gamma_{cat} = 0$ , seems to hold for large cation-cation interaction, too. The data shown in Fig. 4(left) can be fitted with the activation energy dependent on  $\sigma_r$ ,  $\Gamma_{cat}$  and a cross term  $\Gamma_{cat} \cdot \sigma_r$ ,

$$\ln[6 \cdot D_{DC}] = -(a_1\sigma_r + a_2\Gamma_{cat} + a_3\sigma_r\Gamma_{cat}) \quad (12)$$

The slope of the fits in Fig. 4(left) can be expressed according to eqn. (12) as  $a_1 + a_3\Gamma_{cat}$ . Fig. 4(right) illustrates this dependency. The three coefficients turn out to be  $a_1 = 1.41$ ,  $a_2 = 0.063$  and  $a_3 = 0.015$ . The non-vanishing value of  $a_3$  is of particular interest since it contradicts the conclusions of Maass et al. [17]. They showed that for  $c=0.01$  the low temperature behavior is activated, i.e.  $\ln[6D] \propto \frac{1}{T}$  when varying the temperature. Since  $\sigma_r \propto \frac{1}{T}$  and  $\Gamma_{cat} \propto \frac{1}{T}$  this statement is identical to  $a_3 = 0$ . We have included a curve in Fig. 4(left) which represents a variation of the temperature only, this curve shows a proportionality to  $A/T + B/T^2$  ( $A, B > 0$ ). In contrast to this result experimental data for low temperatures show no curvature [17] or opposite curvature [18]. This temperature dependence is also very different to that observed in Coulomb glass for which, if at all, a description with  $B < 0$  would be appropriate for a limited temperature regime in order to recover the Efros-Shklovskii law.

Furthermore we also analyzed the dependency of  $D_{AC}$  on  $\Gamma_{stat}$  and  $\Gamma_{cat}$ . Fig. 5 shows data for  $D_{AC}$  in analogy to those in Fig. 4(left). Exponential fits are not as accurate as for  $D_{DC}$ . Though the data cannot be accurately fitted as straight lines an approximated slope is decreasing with increasing  $\Gamma_{cat}$ . Thus  $D_{AC}$  has a different behavior as compared to  $D_{DC}$ .

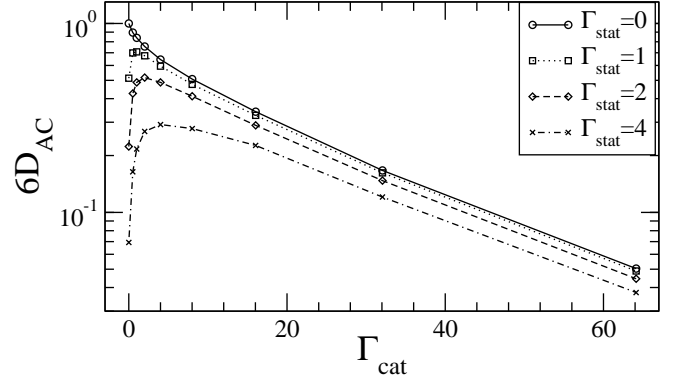


Figure 7: Dependency (CIM) of the high frequency diffusion constant  $D_{AC}$  on  $\Gamma_{cat}$ . The maximum ( $\Gamma_{cat,max}$ ) shifts to larger  $\Gamma_{cat}$  for higher values of  $\Gamma_{stat}$ . The errors are smaller than the symbols.

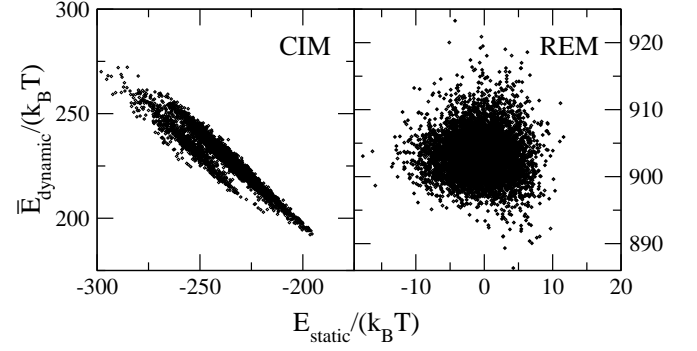


Figure 8: Correlation between static potential and mean value of the dynamic potential for the CIM (left;  $\Gamma_{cat} = 10$ ;  $\Gamma_{stat} = 10$ ) and the REM (right;  $\Gamma_{cat} = 40$ ,  $\sigma_r = 4$ ). Each site is represented by a single diamond symbol ( $20^3$  for each graph). In the CIM a strong correlation is observed, the slope is close to one. In the REM no significant correlation is observed.

The analysis for the CIM was performed in a similar way. The first surprising feature is the increase in mobility of the cations for  $D_{DC}$  (Fig. 6) and  $D_{AC}$  (Fig. 7) when increasing  $\Gamma_{cat}$  from 0 with fixed  $\Gamma_{stat}$ . This is the completely opposite behavior as compared to the REM. Increasing  $\Gamma_{cat}$  further leads to an increase in diffusion until a maximum is reached, from this maximum the diffusion decreases and the slope becomes constant in a logarithmic plot. Obviously, a simple functional form as eqn. (12) can not be found for the CIM. A difference between  $D_{DC}$  and  $D_{AC}$  is that  $\Gamma_{cat,max}$  for  $D_{DC}$  is approximately equal to  $\Gamma_{stat}$  whereas  $\Gamma_{cat,max}$  for  $D_{AC}$  increases more rapidly with  $\Gamma_{stat}$ .

The different behavior of the REM as compared to the CIM can be rationalized by a closer inspection of the differences in the potential surfaces. Comparing Fig. 1 and Fig. 2 and taking the definitions of the models into account it's evident that the static potential of a lattice site in the CIM-surface is spatially correlated, whereas in the REM no correlation among adjacent sites exists. This

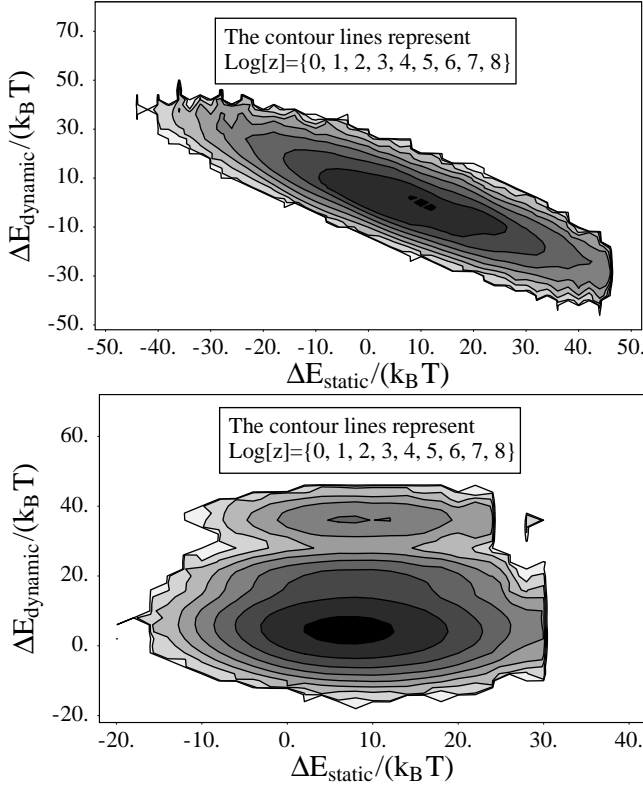


Figure 9: Matrices of successful and unsuccessful trial jumps in the CIM (top,  $\Gamma_{cat} = \Gamma_{stat} = 10$ ) and the REM (bottom,  $\sigma_r = 4$ ,  $\Gamma_{cat} = 40$ ) resolved for static and dynamic jump energies.  $z$  is a counter of how many jumps happen per energy interval during a simulation run. The choice of parameters has no influence on the qualitative picture.

correlation in the CIM has a direct consequence: Fig. 8 illustrates a correlation of the static potential of a lattice site with the mean value of the dynamic potential. For a single starting configuration the static energy of each site is constant during simulation, being denoted as  $E_{static}/k_B T$  in Fig. 8. The mean value of the dynamic energy  $\bar{E}_{dynamic}$  at some site is generated by averaging over all energies which a particle at this site has due to  $H_{cat}$  during a simulation. The observed correlation in Fig. 8(left) indicates a correlation of  $H_{cat}$  and  $H_{an}$ ; high cation-cation energy corresponds to low static energy and vice versa. It could be shown that the three regions observed in the CIM correspond to three different types of lattice sites. There are sites with no, one or two adjacent anions, i.e. anions with a distance of  $\sqrt{3} \cdot \frac{a}{2}$ . No such correlation is observed for the REM.

To elucidate the impact of this correlation on the ion dynamics all occurring trial jumps, accepted or not by the Metropolis algorithm, were recorded during a MC simulation with respect to their static ( $\Delta E_{static}$ ) and dynamic ( $\Delta E_{dynamic}$ ) jump energy differences (Fig. 9). The sum of  $\Delta E_{static}$  and  $\Delta E_{dynamic}$  is the total energy difference for a jump. One apparent effect of the correlation for the CIM is quite obvious: a high energy contribution

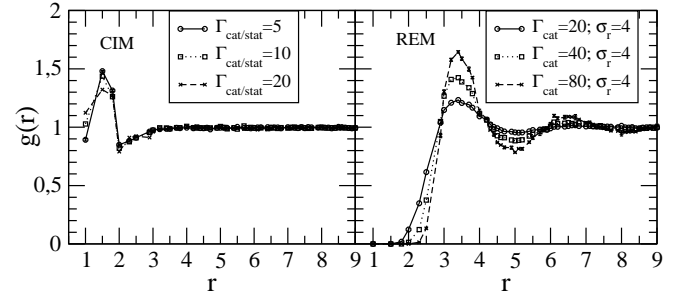


Figure 10: Radial density function  $g(r)$  for the CIM(left) and the REM(right). For the CIM the parameters are chosen to show the temperature dependency and for the REM the dependency of  $g(r)$  on  $\Gamma_{cat}$ . The errors are within the size of the symbols.

from the static energy is accompanied by a low energy contribution from the dynamic energy and vice versa. Therefore to first approximation the total energy does not change during a jump giving rise to faster dynamics. The REM does not show this behavior. For the REM both contributions are independent and both impede the cation dynamics. A consequence is a different jump energy distribution in the CIM as compared to the REM. To further explore the reasons for this behavior the radial density function  $g(r)$  of both models is illustrated in Fig. 10. Obviously, the cations in the REM have a structure, they prefer a certain distance to each other which returns periodically in the graph. This structure is very similar to that found in simple liquid systems. The CIM does not show such a structure, instead it shows an unusual high concentration of cations in very short distances and beyond  $r \approx 3$  the bulk density is already reached. The found structures give possible explanations for the observed behaviors: In the REM each cation is surrounded by a cage of other cations, and this cage slows down the movement [19] because most moves would increase  $H_{cat}$ . In the CIM the cations prefer to populate low energy positions around the anions, which results in an effective screening of the anion charge. This screening flattens the overall energy landscape and thus gives rise to increased mobility. Increasing  $\Gamma_{cat}$  reduces the clustering due to cation-cation repulsion but also supports screening due to higher cation charge. These two effects compete and may account for the observed behavior, see Fig. 6 and Fig. 7.

We are now able to reason the parameter dependency of eqn. (12) for the REM. The first term arises from the static disorder of the energy landscape. The second term is introduced by a cage effect as mentioned above. The cross term on the other hand has no single microscopic origin for  $D_{DC}$  and  $D_{AC}$ . For  $D_{DC}$  it may arise from relaxation of the system to a small perturbation (i.e. a cation jump). By a jump process a cation may have left a well-adjusted environment and is surrounded by an energetically unfavorable environment. Apart from jumping back the total system may also adjust to this new situ-

ation as already formulated in the concept of mismatch and relaxation by Funke [2, 5]. The situation at the new position improves energetically after some time due to the subsequent relaxation of the adjacent particles, thereby reducing the probability of the backjump with time. In the presence of disorder this neighbor relaxation is, of course, much slower since also the neighbors experience the effect of the static disorder. Therefore it is more likely for the central particle to jump back, giving rise to a decrease of  $D_{DC}$  due to the simultaneous effect of static disorder and the cation-cation interaction. For  $D_{AC}$  an increase in  $\Gamma_{cat}$  reduces the dependency on  $\sigma_r$  and therefore the above argumentation fails. For no cation interaction and in the limit of zero temperature the cations occupy only the  $N$  lowest sites in static energy. By introducing cation interaction the emerging liquid structure forces the particles to occupy also some sites which are higher in static energy (but lower in total energy), this would lead to the observed reduction in  $\sigma_r$  dependence.

#### IV. SUMMARY

The REM and the CIM display major qualitative differences in their dependences of  $D_{AC}$  and  $D_{DC}$  on the

system parameters. We gave qualitative reasoning by taking a closer view into the microscopic origins as effects of caging, relaxation, screening and disorder were observed. We have also shown that the conduction in the REM does not show simple Arrhenius behavior and despite their similarities the REM behaves quite differently as compared to the Coulomb glass due to the different nature of trial moves. The results of this work give rise to a new important variable in disordered solids: The spatial correlation of the potential energy hypersurface. Currently we are analyzing the energy hypersurface of real ion conductors to extract this important piece of information.

#### Acknowledgments

We wish to acknowledge the support of the SFB 458 as well as helpful discussions with R. Banhatti, P. Maass and B. Roling. We acknowledge additional support by B. Roling for providing us the Ewald summation program.

- 
- [1] J. C. Dyre, T. B. Schröder, Rev. Mod. Phys. **72**, 873 (2000).
  - [2] K. Funke, C. Cramer, B. Roling, Glass Science and Technology **73**, 244 (2000).
  - [3] N. F. Mott, J. Non-Cryst. Solids **1**, 1 (1968).
  - [4] A. L. Efros and B. I. Shklovskii, J. NPhys. C **8**, L49 (1975).
  - [5] K. Funke, Solid State Ionics **94**, 27 (1997).
  - [6] J. Summerfield, B. N. Butcher, Philos. Mag. B **49**, L65 (1984).
  - [7] J.C. Dyre, Phys. Rev. B **48**, 12511 (1993).
  - [8] J.C. Dyre, Phys. Rev. B **47**, 9128 (1993).
  - [9] M. Pollak and M. Ortuño, *Elektron-Elektron Interactions in Disordered Systems* (North-Holland, Amsterdam, 1985).
  - [10] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984).
  - [11] W. Dieterich, D. Knödler, P. Penzig, J. Non-Cryst. Solids **172–174**, 1237 (1994).
  - [12] D. Knödler, P. Penzig, W. Dieterich, Solid State Ionics **86–88**, 29 (1996).
  - [13] P. Maass, J. Peterson, A. Bunde, W. Dieterich and H. E. Roman, Phys. Rev. Lett. **66**, 52 (1991).
  - [14] N. Metropolis, A. W. Rosenbluth, A. H. Teller and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
  - [15] A.K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectric Press, 1983).
  - [16] P. Penzig, W. Dieterich, Solid State Ionics **105**, 209 (1998).
  - [17] P. Maass, M. Meyer, A. Bunde and W. Dieterich, Phys. Rev. Lett. **77**, 1528 (1996).
  - [18] H. Namikawa, J. Non-Cryst. Solids **14**, 88 (1974).
  - [19] B. Doliwa, A. Heuer, Phys. Rev. Lett. **80**, 4915 (1998).